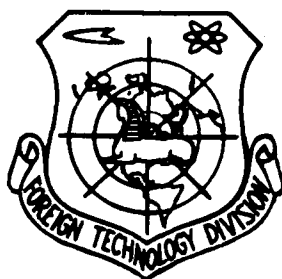AD-A210 698

FOREIGN TECHNOLOGY DIVISION

THERMODYNAMIC PRINCIPLES OF THE PROCESS OF THE EFFECT OF
ELECTROMAGNETIC FIELDS ON A POLYMER MELT

by

V.F. Miroshnichenko, N.I. Semenyuk

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Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*E е*	Ye, ye; E, e*	Х х	*X x*	Kh, kh
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М м	*M м*	M, m	Ь ь	*Ь ь*	'
Н н	*H н*	N, n	Э э	*Э э*	E, e
О о	*O о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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THERMODYNAMIC PRINCIPLES OF THE PROCESS OF THE EFFECT OF

ELECTROMAGNETIC FIELDS ON A POLYMER MELT.

V. F. Miroshnichenko, N. I. Semenyuk.

The effect of electromagnetic fields on a polymer melt leads to an

increase in the strength of polymers [1], while magnetostatic field

virtually does not have an effect on the immobile polymer melt.

However, if relative motion of magnetic field and polymer melt occurs,

then, according to the laws of electrodynamics, besides magnetic field

in the polymer melt appears the electric field, which will interact

with the macromolecules of polymer. As a result of this can be

changed the structure of polymer melt, which will be fixed/recorded in

proportion to cooling fusion/melt, which must immediately be reflected

in the properties of solid polymer.

     Change in structure of polymer melt can be considered as peculiar

phase transitions. Apparently, for the polymer melts besides the

phase transformations of the first and second kind there are other,

possibly, mixed phase transitions [2].

     We experimentally established presence of ΔT-effect in polymer

melts, which is characteristic for phase second-order transformations.

Therefore in this article we use theory of second-order phase

transitions in application to the phenomena in question.

Theoretically everything is reduced to the problem of the study of the transition of polymer melt from the disordered to the regulated state.

Using theory of phase second-order transformations [3], let us record thermodynamic potential near transition point in the following form:

$$\Phi = \Phi_0 = \alpha(T - \theta)\xi + \beta\xi^2 + \ldots \qquad (1)$$

where α and β - constants;

    T - temperature of polymer being investigated;

    θ - transition temperature;

    ξ - coefficient of ordering, equal to n_i/n_0 (n_0 - quantity of disordered macromolecules, n_i - quantity of regulated macromolecules).

Parameter ξ we find from condition of need for existence of stability of system in transition point, i.e., from condition

$$\frac{\partial \Phi}{\partial \xi} = 0$$

This, according to equation (1), it gives

$$\xi = \frac{\alpha(T - \theta)}{2\beta} \qquad (2)$$

Finally, from formula (1) we will obtain expression for the entropy

$$S = S_0 - \alpha S \qquad (3)$$

Formula (2) is temperature dependence of degree of ordering of polymer melt which, analogous with spontaneous relative intensity of

magnetization, is equal to

$$\xi = \eta^2 = \left(\frac{n_i}{n_0}\right)^2$$

Taking into account equation (2), we obtain:

$$\frac{n_i}{n_0} = \sqrt{\frac{\alpha}{2\beta}} \cdot \sqrt{\theta - T} \qquad (4)$$

It is expressed heat of transition of regulated polymer melt through region of transition. At the very transition point the heat is equal to zero $(\Delta S = 0)$. But near the transition point it is possible to determine it as follows. Let us designate entropy in the disordered and regulated state with respect through S_0 and to S. Heat is expressed through the entropies:

$$g_0 = T_0 S_0$$
$$g = TS$$

Difference in heat on both sides of equilibrium curve will be recorded as

$$g - g_0 = \Delta g$$

Taking into account formula (3), we will obtain:

$$-\Delta T = \frac{T\alpha}{c_p - S_0}\xi \qquad (5)$$

In view of the fact that $c_p > S_0$; $T > 0$; $\alpha > 0$; $\xi > 0$, upon transfer of system from disordered to regulated state always must be observed temperature decrease.
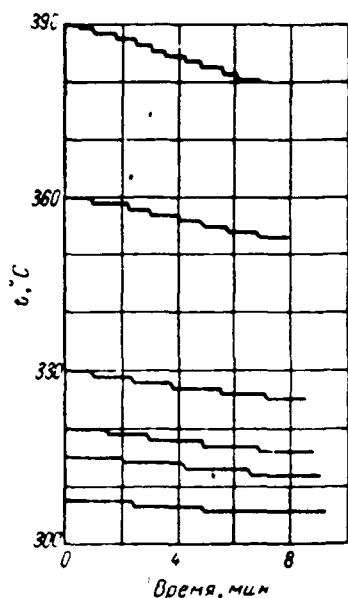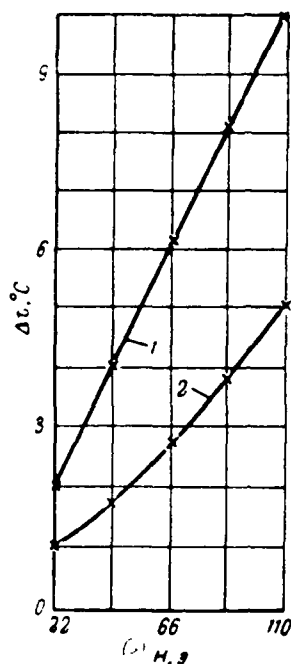
Fig. 1.   Fig. 2.

Fig. 1.   Dependence of ΔT-effect on temperature of fusion/melt of polyethylene.

Key: (1).   Time, min.

Fig. 2.   Dependence of value of ΔT-effect on electromagnetic field strength at temperature of fusion/melt of polyethylene 390 (1) and 335°C (2).

Key: (1).   N, e.

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This phenomenon is named ΔT-effect.   As follows from formula (5), ΔT-effect in this case must be proportional to temperature itself and square of the relative degree of the ordering of polymer melt:

$$\xi = \left(\frac{n_i}{n_0}\right)^s$$

Formula (5) let us rewrite in the following form:

$$-\Delta T = \frac{\alpha T}{c_p - S_0}\left(\frac{n_i}{n_0}\right)^s \qquad (6)$$

As can be seen from formula (6), ΔT-effect must be different depending on multiplicity of regulated macromolecules. In turn, the multiplicity of molecules must depend on the temperature of the polymer melt and strength of the moving magnetic field. It is possible to say relative to coefficient α that it, apparently, determines internal degrees of freedom and, consequently, also the value of ΔT-effect.

Research of ΔT-effect was conducted based on example of high-density polyethylene as follows. The suspension of polymer (10 g) was placed into the test tube, which was fastened in the heating device, a quartz duct with a Nichrome spiral wound around it. This gave the possibility to observe the process of melting visually. Then melting polyethylene with the subsequent heating of fusion/melt to the specific temperature was conducted (for example, to 307°C). After this, polyethylene together with the heating device was placed into the stator of the three-phase asynchronous motor, the strength of magnetic field of which could vary from 0 to 220 Oe, and it is short-time to 300 Oe (in the center of stator). The temperature constancy of fusion/melt was observed during 60-90 min with the

working heating element.   Then field was switched on by
intensity/strength 110 Oe (with the working heating element) and every
15 s was fixed/recorded temperature.   Such measurements for each batch
of polyethylene conducted 6-8 times.   For the new portion of
polyethylene all operations were repeated, but at another temperature
of fusion/melt.

They further investigated dependence of ΔT-effect on
intensity/strength of magnetic field at constant temperature of
fusion/melt.   For this the suspension of polymer (10 g) was placed
into heating device described above and temperature of fusion/melt was
finished to 335°C.   Then fusion/melt together with the heating device
was placed into the same stator of asynchronous motor (in the
turned-off magnetic field), and at the steady current strength of
heating element they maintained the temperature of fusion/melt during
60-90 min.   Then were included fields with intensity/strength 22 Oe
and every 15 s they fixed/recorded a change in the temperature.   After
this, the new portion of polyethylene was finished to temperature of
335°C, but polymer melt was subjected to the effect of the field of
another intensity/strength.

It follows from obtained experimental data (Fig. 1) and formulas
(5) and (6) that ΔT-effect is proportional to temperature of polymer
melt.   The higher the temperature of fusion/melt, the more significant
the ΔT- effect.   Thus, at a temperature of fusion/melt of 390°C
ΔT-effect (temperature decrease) composes 10°C, and at a temperature

of fusion/melt 360°C—7°C. Characteristic is the fact that a temperature decrease occurs intermittently. This peculiar manifestation of ΔT-effect is explained by the fact that the gradual ordering of macromolecules into the complexes with the subsequent addition/connection of other complexes occurs. In this case the higher the temperature of fusion/melt, the less time is required for the complex formation.

This regularity is explained from point of view of melting viscosity of polymers. It is natural that the less the melting viscosity, the more rapidly occurs the ordering of macromolecules and, consequently, also the greater the temperature decrease.

Fig. 2 shows dependence of ΔT-effect on intensity/strength of moving/driving magnetic field. As follows from the conclusions/derivations of thermodynamic theory, ΔT-effect depends on the value of the intensity/strength of the moving/driving magnetic field. And this is confirmed experimentally. The higher the intensity/strength of magnetic field, the greater the ΔT-effect in polymer melt.

Dependence of ratio of value of ΔT-effect to temperature of polymer melt from temperature of fusion/melt is shown in Fig. 3. This relation is the greater, the higher the temperature of fusion/melt. It is natural that the time of the establishment of ΔT-effect depends on the temperature of fusion/melt (Fig. 1).
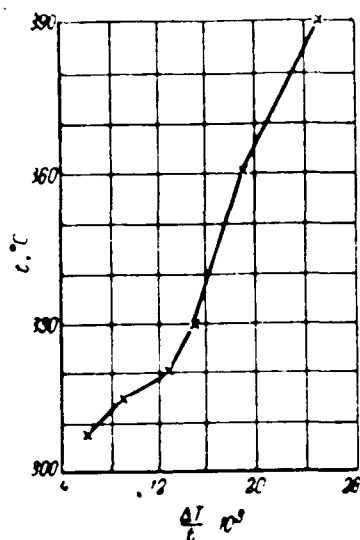
Fig. 3. Dependence of ratio ΔT/t on temperature of fusion/melt of polyethylene.

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